Chapter 7
Microalgal Biomass as a Source of Renewable Energy

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Abstract With the economy destruction and rapid declination of fossil fuels provision, there is an urgent need of low carbon economy generation. Traditional sources of energy have concerns regarding their security and longevity. Searching for fossil fuel energy alternatives is now given more and more attention. Energy produced using micro-algal biomass provides the solution to current dilemma, which not only is renewable source of energy but is environment friendly. Microalgae on account of their high oil composition and rapid biomass generation have great potential for biofuel production and hence have emerged as the most promising raw material for generation of bioenergy. Progress in research methodology for catalytic reactions has gone quite far that has made the efficient conversion of biomass into biofuels possible. Procedures including hydrolysis, followed by trans-esterification, hydrogenation, and isomerization have undergone a great deal of improvement in the last decade from which microalgal lipids have to go through to obtain high-grade hydrocarbons. There are a variety of methods to address microalgal processing suggesting that microalgae are very potent candidates for bioenergy production.

Keywords Biodiesel • Biogas • Bioethanol • Microalgae • Torrefaction

7.1 Introduction

We are living in a world where energy requirements increase everyday. Initially these requirements were met by using fossil hydrocarbons. But fossil fuels are a major source of pollution so there has been a decline in their usage as motor oils due to the progressive introduction of fuel alternatives. Other than that, fossil fuels are also a non-renewable energy source. There is a limited amount of fossil fuels; as we set up more oil fields the older ones get depleted. This also destabilizes the prices of fossil fuels as its demand increases.

Vegetal biomass is now considered as the most important alternative to fossil hydrocarbons. This is because vegetal biomass is produced by consuming solar, geothermal, and wind energy source. Vegetal biomass can be converted into feedstock that can be used as an alternative for oil in industries. Moreover, setting up of large-scale biomass production units can allow us to balance the CO_2 emission with CO_2 absorption. Vegetal biomass causes less environmental pollution than other fuel sources, e.g., coal. Combustion of vegetal biomass yields about 0.2 % SO_2 and 3–5 % ash as compared to coal yielding 2–3 % SO_2 and 10–15 % ash (Sorokina et al. 2012). The reason behind this is fossil fuels contain sulfur, nitrogen, and mineral matter in much higher quantities as compared to the biomass. The most appropriate method of using biomass is by converting it into biofuel. There are various techniques to convert biomass into biofuel; however, the most appropriate biomass-producing crop has not yet been determined. Therefore, it is essential to find an optimum biomass-producing source, which is readily available and highly productive.

There are three generations of biofuels. The first generation uses conventional crops such as soybean, sunflower, and sugarcane as raw material. First-generation biofuels are abundantly produced in the world. The second-generation biofuel production utilizes inedible raw materials such as wood processing and agricultural waste. The second generation is clearly more viable than the first generation as it is abundantly provided and does not utilize edible material. The third-generation biofuel production is associated with the microalgal biomass processing. Microalgal biomass is superior to other bioresources as an energetic raw material. Unlike the terrestrial plants, its growth is more productive and less costly. Some microalgae can yield about 98 m^3 ha^{-1} of high-grade biofuel. Economic calculations show that the cost of microalgal biomass production per year, for an annual output of 100 t, is $3,000. Microalgae are the most quick-growing and highest energy plants. They can provide a basis for industrial scale biofuel production, and therefore, also the sustainable development of future energy economy (Sorokina et al. 2012).

7.2 Overview of Microalgal Biomass Production Techniques

Microalgae nowadays are of significant interest for large-scale production of biofuel because they synthesize useful quantities of triacylglycerides and polysaccharides. These serve as raw material for the production of bioethanol and biodiesel, which can be used as transport fuels.

7.2.1 Cultivation of Microalgae

7.2.1.1 Raceway Pond System

A raceway pond comprises of an oval channel in a closed loop. It is about 0.25–0.4 m in depth and is open to the air. The water containing the necessary nutrients and CO_2 is pumped in a cycle. Due to reduced average light supply in the depth of the pond, raceway pond systems never reach suitable productivity rates. Moreover, the energy cost of pumping water is high.

7.2.1.2 Photobioreactors

Photobioreactors (PBRs) consist of a system of transparent tubes in which the culture medium is enclosed and pumped for circulation from a central reservoir. PBRs are better for controlling algae culture environment, but they are more expensive than raceway ponds.

7.2.2 *Biomass Harvesting*

For large-scale production of biofuel from microalgae, a highly efficient system for harvesting of biomass is required. The techniques that are currently applied in harvesting biomass from microalgae include centrifugation, flocculation, gravity sedimentation, electrophoresis techniques, screening and filtration, and flotation (Uduman et al. 2010).

7.2.2.1 Centrifugation

By the process of centrifugation, a large proportion of microalgae can be removed from culture medium. Chen et al. (2011) mentioned that centrifugation of pond effluent at about 500–1,000 × g shows almost 80–90 % of microalgae removal from culture medium in 2–5 min. Centrifugation is a more preferred method of harvesting the microalgae from culture medium (Grima et al. 2003); however, it can damage the cell structure of microalgal cells (Knuckey et al. 2006).

7.2.2.2 Flocculation

In this process, dispersed particles aggregate to form large particles. These large particles, because of their greater weight, settle down from where they can be easily recovered.

7.2.2.3 Gravity Sedimentation

This technique uses gravitational force for sedimentation of algal cells. Algal cells settle according to their density, radius, and sedimentation velocity. Low-density microalgae are separated unsuccessfully by settling (Edzwald 1993) hence decreasing the efficiency of harvesting.

7.2.2.4 Electrophoresis Technique

Another approach to separate microalgae without any chemicals is the electrolytic method. It involves setting up of an electric field which causes charged microalgae to gradually move out of the solution. Hydrogen generated during the electrolysis of water sticks to the microalgae, which are then carried to the surface (Mollah et al. 2004). The benefits of using this method include:

- Environmental compatibility
- Versatility
- Energy efficiency
- Safety
- Selectivity
- Cost-effectiveness

7.2.2.5 Screening and Filtration

The process involves the introduction of the suspension through a screen of a particular pore size.

7.2.2.6 Flotation

It is a process of separating microalgae using gravitational forces. Air bubbles attach themselves to solid microalgae particles which are then carried to the surface of the liquids.

7.2.3 Cell Disruption

There are two methods for the microalgal cell disruption; chemical disruption and mechanical disruption. Though the mechanical method of disruption requires large amount of energy, still it is preferred over the chemical method because it avoids chemical contamination of cells and does not affect the overall functionality of the cellular content (Chisti and Moo Young 1986; Mata et al. 2010). The microalgal cells can be mechanically disrupted through the processes:

- Homogenization
- Ultrasound
- Milling
- Autoclaving

GEA Process Engineering (2011) states that homogenization can be highly efficient, with a percentage efficiency of about 77–96 %. This means 77–96 % of microalgal cells will be ruptured. But Greenwell et al. (2010) mentioned that for homogenization of 10 L of microalgal suspension having microalgal cell concentrations ranging between 100 and 200 g L^{-1}, we would require a high amount of energy of about 1.5–2.0 kWh.

Another mechanical disruption method is sonication. It involves applying ultrasound ranging between 20 and 50 kHz to the sample. The frequency is generated electronically and the energy is transferred to sample mechanically via a metal probe. The high frequency generates an area of low pressure. The microalgal cells move towards the area of low pressure. This area of low pressure has the highest impact of ultrasound frequency which ultimately breaks open the cell.

7.2.4 Compound Extraction

The extraction of lipids from the microalgal can be done on cryodessicated material efficiently (Fajardo et al. 2007). Ninety-six percent ethanol is used for the extraction of lipids from lyophilized biomass. A system having two phases is formed by the addition of hexane and water to the extracted crude oil. The purified lipids are then transferred to the hexane phase. Majority of the impurities get left behind in the aqueous phase.

Carbohydrates present in microalgal cells are of much complex nature and consist of neutral sugars and amino sugars. Carbohydrates found in the microalgal biomass can be quantified by using phenol–sulfuric acid. The sugars are first hydrolyzed to furans, which are then quantified by spectrophotometry. The carbohydrates can be extracted by chromatography and acid hydrolysis. Other than that, cell walls of microalgae can also be hydrolyzed for the production of reducing sugars by using cellulase (Fu et al. 2010).

7.2.5 Fractionation and Purification

Microalgal biomass includes lignocellulosic components. Lignocellulosic components are a resource of relatively low value but they can be used for the production of fuels and help us meet the present fuel and energy requirements. Research and development of biorefining technology is ongoing. One of the approaches is the pretreatment of raw microalgal biomass, resulting in its fractionation into separate biopolymers, which are mainly lignin, hemicellulose, and cellulose. The cellulose content obtained through this approach can be hydrolyzed easily for obtaining simple sugars.

7.3 Microalgal Strains for Bioenergy

The world's energy consumption rate increases day by day due to an ever-increasing population and the overall desire for a better living standard. This consumption rate of energy usage combined with the knowledge of the threat that carbon dioxide poses on the climate has led many researchers, scientists, and environmental engineers to study the potential of biofuels as an alternative to overcome the problems caused by pollution. Among the potential biofuel sources, microalgae are considered as the most efficient. Microalgae are the most adaptable and sustainable energy source.

Bioenergy production from microalgae is believed to be one of the most efficient alternatives for the development of CO_2-neutral fuels for several reasons:

1. Microalgae have the most suitable growth rates for biomass production.
2. They have a higher efficiency of photon conversion which results in a higher biomass yield per unit of surface.
3. They can synthesize and accumulate large quantity of neutral lipids.
4. They can (under specific growth conditions) release hydrogen.
5. They can provide additional benefits of wastewater bioremediation.

One friendly way of producing energy is the production of photobiological H_2 using *Chlamydomonas reinhardtii* (a microalgal strain). Other microalgal strains that can be used include *Chlorella vulgaris*, *Phaeodactylum tricornutum,* and *Nannochloropsis* species.

7.4 Conversion of Fatty Acids into Bioenergy

The conversion of fatty acids obtained from microalgal biomass into biodiesel for the production of energy is done by transesterification process. Transesterification is a chemical reaction through which fatty acids are bonded to alcohol, resulting in the production of methyl esters of fatty acids commonly known as fatty acid methyl esters (FAME) and glycerol. FAME basically is biodiesel. This process reduces the viscosity of fatty acids and makes them combustible (Chisti 2007).

For the transesterification process, one mole of alcohol is used to transesterify one mole of esters. Likewise, for the transesterification of one mole of triglyceride, 3 mol of alcohol is used (Fukuda et al. 2001). This process is a reversible reaction, therefore, for a high yield, 6 mol of methanol are used for each mole of triglyceride. This large excess ensures the reaction is driven in the direction of FAME (Fukuda et al. 2001).

The transesterefication process can be catalyzed by acids, alkalis, lipase enzymes, and microwave heating.

7.4.1 Acid-Catalyzed Transesterification

The process is driven to completion by the large excess of methanol. In the presence of a large excess of methanol, the free fatty acids are rapidly transesterified into methyl esters at a temperature of about 80 °C. The molar ratios and temperature are the most significant factors affecting the yield of FAME (Zheng et al. 2006).

7.4.2 Alkali-Catalyzed Transesterification

It is about 4,000 times faster than the acid-catalyzed transesterification (Fukuda et al. 2001). It involves the use of sodium and potassium hydroxides as commercial catalysts. An even better catalyst such as sodium methoxide is also used, but sodium hydroxide and potassium hydroxide are often chosen for their cost. Water presence can cause base hydrolysis so the reaction is kept dry. The optimum conditions for the alkali-catalyzed transesterification include atmospheric pressure and a temperature of around 60 °C. In these conditions, the reaction is completed in approximately 90 min (Chisti 2007).

7.4.3 Lipid-Catalyzed Transesterification

Nowadays, the lipase-catalyzed transesterification for FAME production is of great interest. The use of lipase enzymes does offer many important advantages, but is not yet feasible because of the high cost of the catalyst (Fukuda et al. 2001).

7.4.4 Microwave Heating

Microwave heating can also be used for speeding up the transesterification process. This process uses additional catalysts such as scandium triflate and bismuth triflate. Upon providing a temperature of 150 °C by microwaves, the reaction is completed in about 20 min (Sochaa and Sello 2010; Levine et al. 2012).

7.5 Converting Carbohydrates into Bioenergy

Algae mostly do not contain simple carbohydrates or easily hydrolysable polysaccharides. Most commonly found carbohydrates in algae are mannanes, cellulose, ulvan, fucans, xylanes, alginic acid, agarose, porphyran, furcelleran and funoran, mannitol, and laminarin. Starch and cellulose are only present in minor quantities. The yield of ethanol production from biomass is dependent upon the presence of fermentable sugars. Algae have only a low level of fermentable sugars, most of the microalgal biomass is lignocellulose which, as mentioned earlier, is a low value resource but it can replace petroleum by providing fuel and energy.

The lignocellulosic components, which are present in microalgal biomass, can provide fuel and energy. One biorefining technique is the pretreatment of raw microalgal biomass. This enables us to obtain biopolymers such as lignin, hemicellulose, and cellulose. The cellulose content obtained through this approach can be hydrolyzed easily for obtaining simple sugars.

Carbohydrates present in the microalgal biomass are converted into bioethanol for bioenergy production by the biochemical conversion of carbohydrates into ethanol. This can be done in two different ways:

7.5.1 Anaerobic Digestion

It is the introduction of microorganisms in an oxygen-free environment for the breakdown of organic material, which in this case is carbohydrate. Anaerobic digestion is a multistage process and is mostly used for methane gas production and carbon-rich biogas production. In the first stage, microorganisms breakdown complex carbohydrates into simpler ones. In the second step, the simpler carbohydrates are anaerobically metabolized into alcohols, mainly ethanol and CO_2. If the reaction progresses further, ethanol is metabolized into methane gas and CO_2.

7.5.2 Fermentation

At its most basic level, fermentation means the use of yeasts to convert carbohydrates into alcohol, notably ethanol, also called bioethanol. Ethanol production from cellulose by fermentation is more complex than conversion of carbohydrates and starch components of microalgal biomass. Lignocellulosic biomass must first be broken down into simpler sugars before being fermented into ethanol. The components of lignocellulose (cellulose, hemicellulose, and lignin) have strong chemical bonds and are difficult to separate. Mechanical pretreatment and enzymatic treatments are necessary for the breakdown of lignocellulose (Zhao and Shengdi 2013). After the breakdown, the resulting carbohydrates are fermented into bioethanol.

7.6 Processing Techniques Involved in Bioenergy Production/Biomass Conversion Technologies

Bioenergy is the energy made available from biological resources and is renewable in nature. One way to get this bioenergy is from biomass obtained from microalgae. The key to the production of bioenergy from microalgal biomass depends upon identifying the best strain and the separation of biomass from the oil. There are several techniques used for the conversion of biomass obtained from microalgae into bioenergy. Some of these techniques or processes are:

7.6.1 Gasification

Gasification is one of the best-proven methods for the production of bioenergy from microalgal biomass. Gasification comes under the category of thermochemical conversion, which involves breaking the organic components of biomass thermally (Tsukahara and Sawayama 2005) and is an exothermic reaction. In this method (Gasification), partial oxidation of biomass is carried out at high temperature of approximately 800–1,000 °C, yielding a combustible gas mixture (Clark and Deswarte 2008). During the process, a combustible mixture of gases containing CO, CO_2, H_2, NH_2, and CH_4 is produced by the reaction of water and oxygen with the microalgal biomass (Demirbas 2001). This mixture of gases is called Syngas or Producer gas. Syngas can be cleaned and used in gas engines as a fuel and turbines and can also be burnt directly (McKendry 2002a) or it may be upgraded to liquid fuel or chemical feedstock by biological fermentation (Datar et al. 2004). Two of the microalgae that have been mentioned in the literature to produce bioenergy are *Spirulina* (Arthrospira) and *Chlorella vulgaris*. The work on *Spirulina* was carried out by Hirano et al. in 1998 in which they partially oxidized the micro algal specie at 800–1,000 °C and that on *C. vulgaris* by Minowa and Sawayama in 1999 in which they gasified algae with nitrogen cycling in a novel system to obtain fuel rich in methyl (Brennana and Owendea 2010).

7.6.2 Pyrolysis

Pyrolysis is one of the other simple conversion methods to produce bioenergy from microalgal biomass. It basically means the thermal cracking or decomposition of biomass. It is carried out at lower temperature of 400–500 °C as compared to gasification and is endothermic in nature. It yields a heterogeneous mixture of solid, liquid, and gaseous intermediates and occurs without oxygen unlike the process of gasification. The liquid content also called bio-oil or pyrolysis oil resembles a very viscous tar and can be upgraded to fuels (and can be used as a motor fuel but only after removing oxygen from it) or chemicals because of its high oxygen content and alkalinity and fuel can be obtained by solid part (char) or it can be used for soil amendment (Field et al. 2013). Pyrolysis is further divided into fast and slow pyrolysis. Fast pyrolysis produces bio-oil or pyrolysis oil and takes a few seconds to minutes, while the slow pyrolysis takes minutes to days for completion and is aimed at producing solid part also called as char (Babu 2008). However, there is a problem with pyrolysis that creates an urge to upgrade pyrolysis oil to lower oxygen content and remove alkalis because it is unstable with acidic nature and dissolved solids (Chiaramonti et al. 2007). In 2004 Miao and Wu used fast pyrolysis to produce bio-oil from heterotrophic microalgae *Chlorella protothecoides*. They found that the bio-oil produced had a low amount of oxygen, low viscosity, high heating value and lower density as compared to biofuel obtained from autotrophic species and wood.

7.6.3 Direct Combustion

Direct combustion is one of the other very important thermochemical conversion techniques used for producing bioenergy from microalgae. According to Gaul (2012), it is one of the most dominant processes used for the production of bioenergy worldwide. Direct combustion is usually carried out in a furnace or a boiler in which biomass is directly burnt in the presence of air (O_2) to produce hot gases which are formed because of the conversion of stored chemical energy in the biomass and these hot gases can then be used to produce bioenergy. It involves the heat production accompanied with the production of CO_2 and H_2O from the oxidation of biomass rich in carbon and hydrogen. But this process like others also has some issues, which makes it a bit unsuitable. Firstly the direct combustion of biomass needs some pretreatment of biomass like drying, chopping, and grinding which increases the production cost as well as more energy is utilized (Goyal et al. 2008). Secondly if the combustion is not carried out properly means that in case of imperfect combustion, there is a production of intermediates and some environmental pollutants like CH_4, CO, and particular matter (Tanger et al. 2013). Thirdly the fuel production associated with direct combustion has fuel impurities. It contains sulphur and nitrogen, which causes the emission of sulphur and nitrogen oxides SOx and NOx, respectively, (Robbins et al. 2012).

7.6.4 Transesterification

Transesterification is a process in which "R" group of an ester gets exchanged with the "R" group of an alcohol in an acid/base-catalyzed reaction. It can be used for the production of bioenergy from microalgal biomass. The lipid content in particular the triglyceride content of algal biomass reacts with alcohol in the presence of a catalyst resulting in the formation of biodiesel. The reaction is characterized by the replacement of "R" group of triglyceride with the OH of alcohol particularly methanol resulting in the production of methyl esters (biodiesel). In an experiment carried out by Hossain et al. (2008) and his colleagues, the production of biodiesel from two species that are *Oedogonium* sp. and *Spirogyra* sp. was compared. They showed that the percentage of algal dry weight was higher in *Oedogonium* sp. as compared to the *Spirogyra* sp. before oil extraction but after oil extraction it was higher in *Spirogyra*sp. On the other hand, the extracted oil and biodiesel production both were minimum in *Spirogyra* sp. and maximum in *Oedogonium* sp. Johnson and Wen (2009) worked on algal specie *Schizochytrium limacinum*. The purpose of their experiment was to observe the potential of biodiesel production from this algae using two different methods; the first one involving oil extraction followed by transesterification (two-step process) and the second one involving the direct transesterification of algal biomass (one-step process). Their results indicated that the one-step process of direct transesterification of algal biomass resulted in high yield of crude-biodiesel as compared to the two-step process depicting that the algae *Schizochytrium limacinum* is a good feedstock for the production of biodiesel via direct transesterification.

7.6.5 Hydro Cracking

Hydro cracking is a catalyst-associated reaction that is mostly used for the separation of petroleum products. It is assisted by an elevated partial pressure of hydrogen gas, which purifies the hydrocarbon stream from sulphur and nitrogen hetero atoms. But products of microalgal hydro cracking are different from those of petroleum products, so for hydro cracking of microalgae a different set of catalysts is needed that is able to withstand elevated temperatures and pressures as well as high water and phosphate contents (Sorokina et al. 2012).

7.6.6 Biochemical Conversion Technologies

Biochemical conversion is the biological process to convert biomass into bioenergy using methods such as anaerobic digestion, alcoholic fermentation, and photo biological hydrogen production.

7.6.6.1 Anaerobic Digestion

It is the conversion of algal biomass into biogas. The biogas consists primarily of methane and CO_2 with the traces of gases such as H_2S. This sort of reaction occurs in digesters where organic biomass is broken down to produce biogas in a series of three successive steps including hydrolysis, fermentation, and methanogenesis. During hydrolysis the complex organic mass is broken down into soluble sugars which is then fermented into alcohols, acetic acid, and volatile fatty acid along with the gas containing hydrogen and carbon dioxide which is then converted into methane by methanogens in the last step of methanogenesis (Cantrell et al. 2008). This method not only produces high amount of energy, but also leaves a waste rich in nutrient that can be used again as a new medium for algal growth (Olguín et al. 2000). But there is one problem with this process too that is the microalgae that have a high protein content result in low C/N ratio thus affecting the performance of digester. In 2007, Yen and Brune presented a solution to this problem by adding waste paper with a high carbon content to algal biomass resulting in a high C/N ration and consequently doubled the amount of produced methane as compared to pure algal biomass.

7.6.6.2 Alcoholic Fermentation

It is the simple conversion of sugars in the biomass of algae into ethanol. The sugars of the biomass are mixed with yeast and water in large tanks called fermenters. The yeast converts the sugars in the biomass to ethanol (McKendry 2002b). The product obtained then passes through a distillation process that removes the water and other impurities and gives concentrated alcohol, which is then condensed and can be used as fuel for cars. The solid by-product of the reaction can be utilized for gasification or cattle feed. Ueno et al. in 1998 investigated the production of ethanol by microalgae *Chlorococcum littorale* using dark fermentation under anaerobic conditions. They found that 450 μmol g^{-1}-dry wt. was the highest productivity of ethanol at 30 °C.

7.6.6.3 Photo Biological Hydrogen Production

H_2 is one of the important molecules and is an efficient energy carrier and microalgae can photoproduce it because they possess all the metabolic, genetic, and enzymatic characteristics to produce it. There are fundamentally two approaches to produce hydrogen gas from microalgal, one of them is a two-step process while the second is simultaneous production of hydrogen. In the two-step process, the microalgae are first grown photosynthetically under normal conditions and in the second stage they are grown anaerobically by depriving them with sulphur and hence starting consistent production of hydrogen gas (Melis and Happe 2001). In the second approach called the simultaneous production of H_2, the electrons produced from the photosynthetic reduction of water are acted upon by hydrogenase to produce H_2. Although the yield of hydrogen gas is greater in case of simultaneous production process, this productivity is limited by the inhibition of hydrogenase by oxygen produced from photosynthesis.

7.7 Torrefaction

No doubt algal biomass is a good source for the production of renewable energy, but there are certain properties of biomass that are unsuitable. These include high moisture content, low calorific value, high oxygen, and its fibrous nature, which make the process control more complex. To improve the biomass properties and avoid the above-mentioned problems, scientists developed the process of torrefaction.

Torrefaction is a thermal conversion process operating at a low temperature of 200–300 °C. It is also called as mild pyrolysis, roasting, and high temperature drying and is carried out in the absence of oxygen (Stelta et al. 2011). Torrefaction is like pretreatment of biomass. It reduces the oxygen content of the biomass, increases the calorific value of biomass, and also destroys its fibrous nature. One of the other benefits of torrefaction is that after torrefaction the hydrophobic nature of the biomass is enhanced which makes the storage of torrefied biomass easier than non-torrefied one. The torrefaction process is divided into five main stages, which are: (1) Initial heating, (2) Pre-drying, (3) Post-drying, (4) Torrefaction, and (5) Solids cooling (Stelta et al. 2011).

- *Initial heating*: In this stage the biomass is heated. The temperature is increased in the start and moisture starts to evaporate at the end of this stage.
- *Pre-drying*: The water is evaporated from the biomass at 100 °C.
- *Post-drying*: Biomass is heated to 200 °C. All the water is released and some loss of mass occurs.
- *Torrefaction*: During this stage the actual process of torrefaction occurs.
- *Solids cooling*: In this stage the torrefied material is cooled below 200 °C.

7.8 Emerging Pathways for Microalgal Biofuel Production

With the increasing rapid reduction in the amount of fossil fuels and the increasing demand of the biofuel, new pathways are emerging to produce biofuel with better quality and quantity. In this regard, three of the emerging pathways for the production of biofuel from algal biomass are being explained. All these processes have the same goal to produce better biofuel, but they differ in their lipid extraction method and end products. These processes have the advantage of increasing the biodiesel yield, net energy ratio, and better environmental performance.

7.8.1 Hydrothermal Liquefaction

Hydrothermal liquefaction also called thermochemical liquefaction is a process that involves the production of liquid fuel directly from the wet algal biomass (Patil et al. 2008). It is a high pressured and low temperature reaction which usually occurs at 5,000–20,000 Kpa (Kilo pascal) and 300–350 °C in the presence of catalyst to yield bio-oil (Goyal et al. 2008). Thermo-chemical conversion can have advantage over direct combustion because it does not involve pretreatment especially drying of the biomass, which saves a lot of energy, but, on the other hand, the reactor system for thermo-chemical conversion is expensive. Minowa and his colleagues carried out experiment on *Dunaliella tertiolecta*. They found that the algal cells of *Dunaliella tertiolecta* with a moisture content of 78.4 wt% yielded about 37 % oil on organic basis when they were thermally liquefied at 300 °C and 10,000 Kpa.

7.8.2 *Oil Secretion*

The method of oil secretion basically aims to cultivate microalgae such that they will secrete the oil. The media is taken out of the photobioreactor and oil is recovered using conventional oil and water separator. The biomass is harvested in the same way as for other processes. The biomass is then anaerobically fermented in the digester producing liquid and biogas. The biogas is burnt and the liquid digestate is then recycled so that the nutrients can be reused (Delruea et al. 2013).

7.8.3 *Alkane Secretion*

The model for the alkane secretion process is very similar to that of oil secretion. In this process, phase separation is carried to separate the secreted alkanes from the cultivation media. This retrieval of alkanes is performed in an oil water separator. The difference between the density of alkanes and the media allows this separation. According to one hypothesis, these secreted alkanes can be used directly in motors. This sort of approach saves the energy, which may be utilized for upgrading and refining of the products (Delruea et al. 2013).

7.9 Biorefinery Concept for Biofuels and High Value Products

"Bio refinery" depends on the idea of petroleum refineries, which produces number of fuels and end products from crude petroleum. Biorefinery merges various processes and apparatuses to generate power, biofuels, and high value biomass chemicals. It strives towards processing of sustainable biomass into an array of commercialized energy and products (Demirbas 2009).

Following are the steps involved in biomass production through microalgae and microalgal-based biorefinery: microalgae cultivation, harvesting of biomass, disruption of cell, compound extraction, fractionation, and purification. The main gist of this theory is to dissuade and recover the desirable compounds from the same biomass batch, in order to produce intact commercialized products. One of the major bottlenecks of the biorefinery concept is the fractionation step, as it is hard to separate various compounds without causing any damage to other fractions (Vanthoor-Koopmans et al. 2013).

The main compounds having grave importance produced from microalgae are lipids, carbohydrates, and proteins. Microalgae lipids are of interest because they have essential fatty acids, e.g. ecasopentoic acid (EPA) and docasahexanoic acid (DHA), which are not present in food crops and other various fatty acids (omega-3, γ-linolenic acid, etc.). For biodiesel production, lipids can be used as feedstock.

Certain catalyst and alcohol are required for the conversion of lipids into biodiesel (fatty acids methyl esters FAME). However, neutral lipids (triacylglycerides TAGs) are only suitable for this purpose.

Nowadays optimization of conditions for microalgal production abundant in lipids is the main focus. Carbohydrates are also preferred as feedstock for various biological biomass conversion technologies, especially for fermentation technology of sugars for bioethanol production. When microalgal cells are cultivated under stress conditions, both lipids and carbohydrates make up to 60–65 % dry weight associated with abiotic factors like salinity, temperature, nutrient starvation/limitation, and light intensity.

Proteins produced through microalgae are also of vital importance as their nutritional quality is comparable to other food proteins because of their good amino acids proportion and profile. It seems that main biomass composite are total proteins that lower significantly during stress conditions where lipids and carbohydrates are built up. Methods that are involved in conventional purification of proteins include precipitation of aluminum sulphate, precipitate formation, salting out, chromatography, and electrophoresis, which are assumed to be cost and time-consuming and affect the protein activity. Extraction of microalgal high value and bioactive compounds can be done through a number of methods used in general for plant bioactive compound extraction (Becker 2007).

In biorefinery concepts under mild conditions, the co-extraction and separation of proteins and lipids through ionic liquid method seems very promising. Biorefinery done through microalgae is at initial stages and research is needed on this topic (Lin et al. 2013). When the desired compound or compounds are extracted, the remaining leftover biomass can be utilized by any of the conversion technologies for biomass energy like anaerobic fermentation, digestion, liquefaction, etc. for the production of biofuels. For example, *Nanochloropsi*s sp. can be utilized for pigment and lipid extraction and unexploited biomass can be used for the production of bio-hydrogen through dark fermentation. Biomethane can be produced using residues of biomass of feedstock microalgae after lipids extraction (Serive et al. 2012).

7.10 Problems Associated With Bioenergy Generation from Microalgal Strains

Nowadays, biomass production through microalgal strains is still not a realistic option for intake as synonymous to the current terrestrial crops for energy production. On the basis of many LCA studies, the efficiency ratio of conversion of energy obtained through microalgae is consequentially lesser than oil extracted from palm, jatropha, and rapeseed indicating untenable production of microalgal biofuel. In the overall microalgal process chain, several energy hotspots are identified including harvesting/dewatering of microalgal biomass, photobioreactor operation, and production of inorganic nitrogen source. It is advised that microalgal culture for biofuel generation should be treated with wastewater to downgrade the heavy dependence on the nutrients extracted from inorganic nutrients. Protein extraction and separation are difficult as they have poor stability and are denatured under acid, alkali, or high temperature. On the other hand, in biorefinery it is vital to build up a technique that enables extraction of an array of metabolites considering the hardness of extraction, their inaccessibility, and/or wide range of polarities.

Lipid extraction through microalgae in the downstream process represents a difficult task. Method of Physical Extraction utilized in the oil extraction from oil-bearing crops is not up to the mark in the extraction of lipids through microalgae as the lipids are integrated within the cell wall layer. In disruption methods of cell, precautions should be taken to check the energy level as it deviates very easily towards the negative balance. It should be added that the choice of cell disruption methods, extraction conditions, and largely chemical solvents are based upon strains of microalgae. For optimum extraction of lipids, there is no singular method for all types of strains of microalgae. To improve the microalgae production of biodiesel, several breakthrough technologies, i.e. in situ transesterefication, surface extraction/transestererification, hydrothermal recovery, and transestererification coupled with ultrasonic and microwaves, are still to be ascertained. Many strategies utilized to strengthen this biofuel production require extensive research. To gain significant breakthrough we need progress in this area as to produce greener, sustainable, and stable biofuel.

7.11 Economic Feasibility of Microalgae to Biofuel

A wide range of bioactive compounds of high value to be utilized as natural resources, pigments, pharmaceutical compounds, polysaccharides fatty acids, and health foods can be obtained through microalgae. Through a high value coproduct strategy, economic usability or possibility of biofuel production through microalgae can be significantly improved. It involves production of microalgae passing through certain stages in a farming facility of microalgae (CO_2 mitigation), from harvested algal biomass extracting bioreactive products processing through thermal energy (gasification, pyrolysis, or liquefaction), different applications reforming biofuels and from resulting liquid, vapor, or solid phases extracting high value chemicals. By applying high value coproduct strategy integrated with biorefinery, we can upgrade significantly the collective cost-effectiveness of production of biofuel through microalgae (Sorokina et al. 2012). Other than some microalgal compounds, which are already produced at commercial level, most of the high value compounds, which are produced by microalgae, are not built up in the market for high value products produced through microalgae (Brentner et al. 2011).

Commercially used carotenoids are estimated on the current global market in 2010 at $1.2 billion, with a probability to grow to $1.4 billion in 2018 with 2.3 % compound annual growth rate. β-carotene market value is estimated in 2010 at $261 million and is expected to grow to $334 million by 2018 with 3.1 % compound annual growth rate while the commercial value of lutein was about $233 million in 2010 and is estimated to peak by 2018 to $309 million with 3.6 % compound annual growth rate. Use of bioplastics was 0.64 Mt globally in 2010 and 0.85 Mt in 2011 and is expected that their use will rise up to 3.7 Mt by 2016 with 34.3 % high compound annual growth rate. In 2011, global demand of glycerol was 1,995.5 Kt and is estimated to rise to 3,060.4 Kt by 2018, while the worldwide supplement and vitamin market is about $68 billion.

Besides the constraint of utilization of water, nutrient and occupation of land, concept of cultivating biomass through microalgae for high value chemicals generation linked with the production of biofuel to accumulate world's needs for means of transportation is massive pressure (Markou 2012). One consequence is the overuse of high value microalgal products in the global market. It is estimated that the production of bioethanol and biodiesel will double between 2007 and 2017 touching 125 and 24 billion liters, respectively. By taking assumptions that the activity of biomass produced through microalgae to the production of biofuel might be 30 % and that the yield of biodiesel is 0.30 L kg^{-1} while that of bioethanol is 0.25 L kg^{-1} both of which are dry microalgal biomass, an initial assumption of the biomass produced through microalgae in the global annual scale is 175 million tons of dry biomass per annum covering a surface of about 2–9 Mha (estimating a yield of microalgal dry weight biomass 20–100 tha^{-1} yearly).

7.12 Biodiesel, Biogas, Bioethanol Production from Microalgae

7.12.1 Biodiesel

Fatty Acid Alkyl Esters, which is a constituent of biodiesel, is another source of diesel fuel extracted from the reaction of vegetable oils or lipids and alcohols with or without the help of a catalyst. Transesterification is the process through which oil is converted into fatty acids (biodiesel) (Chisti 2007). Biodiesel acts as a biodegradable alternative fuel, which is nontoxic and derived from renewable sources. Biodiesel is produced in many countries from soybeans, palm oil, corn oil, and canola oil. The animal fat and waste cooking oil are other sources of biodiesel production in the commercial market. But modern research and experimentation have proven that through microalgal cultivation, biodiesel production is truly superior to all other forms and has the potential to make fossil fuel utilization completely extinct. Algae are cosmopolitan and have dry mass weight of in between 20 and 80 % oil weight. They have much rapid growth rate than terrestrial crops. It is estimated that oil production yield from algae ranges from 20,000 to 80,000 L per acre per year. It is 7–31 times better than the next best crop, palm oil. Due to their easy compliancy and acclimation to the conditions of growth, the use of algae as energy crop has possibilities. Because of the research done in this field, it is proved that the oil produced through algae can be an important source of biodiesel. Many different species are better suited for the production of different types of biofuels. Algae has emerged as having the highest potential for biodiesel production. Processes for the production of biodiesel through microalgae include a bioreactor for producing large amount of microalgal cells, next is the separation of cell from the growing medium and then extraction of lipids (Chisti 2007). Those algae, which produce greater lipid content would be ideal for biodiesel production. By medium alterations, lipid content can be enhanced. Lower nitrogen source in the medium causes greater deposition of lipid in the cell. At lower cell density, nitrogen would have worked up earlier, when the starting concentration in the medium was low. Through this, cell can accumulate lipid in their cell when there is a good injection of light, resulting in excess metabolic flux produced through photosynthesis on a unit biomass basis. In addition to the concentration of nutrient, condition of culture also plays a vital role, i.e., light, temperature, pH and CO_2 concentration (Huang and Chen 2010).

After cultivation of microalgae, harvesting of biomass is the next. It can be produced through sedimentation microscreen centrifugation, flocculation, or filtration of membrane. It is required to be dried by releasing water. To get oil, dried biomass is extracted through vacuum. Then the oil is passed on to the biodiesel production unit (Ahmad et al. 2011).

7.12.2 Biogas

Biogas includes both methane and hydrogen gas and it can be extracted by the exploitation of microalgae through many processes and steps. Exploitation of solar energy photosynthetic spectrum can be utilized to produce chemical energy through microalgae complemented by bacteria to prepare methane. In the process, mass production of algae is done through light and carbon. The algal biomass serves as a source of sustenance for anaerobic digester feeding by using anaerobic bacteria for producing methane. For algal biomass production, the source of carbon can be wastewater for eukaryotic algae and through atmosphere or from exhaust gases combustion of both prokaryotic and eukaryotic algae (John and Anisha 2011). Many micro- as well as macroscopic algae can be used for the production of biogas. It is proven by the data of technical feasibility on anaerobic digestion of biomass from algae. For example, biomass can be utilized from macroalgae, green alga *Ulva lactuca*, red marine alga *Gracilaria*, and giant brown kelp *Macrocystis pyrifera*. Some of the microscopic alga, which can be successfully utilized for methane production are mixed culture of *Chlorella* spp. *and Scenedesmus* spp., mixture of *Euglena* spp., *Chlorella* spp., *Oscillatoria* spp., *Scenedesmus* spp., and *Synechocystis* spp., *Scenedesmus* spp. culture only and together with either *Euglena* spp., *Spriulina* spp., *MIcractinium* spp., *Melosira* spp. *or Oscillatoria* spp., the mixture of *Hyddictyon reticulatum and Cladophora glomerata*.

Hydrogen gas is considered to be a fuel ideal for the world in which air pollution has been accumulated to arrest global warming in an economically sustainable manner. Thus, H_2 gas is evolving itself as a fuel of the future to the carrier of energy nowadays. However, none of the production processes currently available can economically produce renewable H_2 gas, i.e., photovoltaics-electrolysis and biomass gasification can yet generate hydrogen fuel for less than US$20/G.I., which is a realistic target for renewable H_2 gas maximal cost (Harun et al. 2009). There is an increased interest for renewable H_2 gas through microalgae. Many countries of Europe, United States, and Japan have done extensive research on microalgal cultivation for H_2 gas production. The concept of process for the production of biohydrogen is based on the formation of protons from direct transfer of electrons from water by coupling the water splitting photosynthesis reaction of reduction of ferrodoxin to a H_2 evolving hydrogenase; a process now known as "direct bio photolysis." "Indirect biophotolysis" is another process, which utilizes adapted green algae anaerobically. It involves oxygen evolving through spatial separation and reactions producing H_2 coupled through CO_2 intermediate fixation into carbohydrates. A variation is to utilize microalgae to make organic substrates through fermentation that are changed into H_2 by photosynthetic bacteria. Both of these processes are of great importance in applied phycology and energy production through microalgal biomass.

7.12.3 Bioethanol

The increasing industrial and social awareness of the impact of fossil fuels and their rising cost have established a necessity for more stable options of fuel. Production of renewable bioethanol from biomass consistent of starch and sugar materials is considered to be one of many possibilities and it is nowadays being produced significantly (Pienkos and Darzins 2009). Outburst of population coupled with increasing influx of motorization has pointed us the demand of large amount of fuel. In this age of environmental as well as economical concern, algae having the potential of accumulation of increased cellulose/starch storage can act as an effective alternative to crops that provide food for the production of bioethanol. For a sustainable future, it can act as a green fuel. Some of the species of algae can make ethanol during a process called dark anaerobic fermentation and thus can act as a source for the production of ethanol. As of late, microalgae that are oleaginous can produce large cellulose/starch biomass waste that can be used for the production of oil, which can be then run through hydrolysis to make syrup rich in sugar to serve for ethanol production as substrate (Radakovits et al. 2010).

Use of ethanol as an additive of fuel or as source of fuel directly has been increased significantly due to the regulations imposed by the government and in several cases as incentives implemented because of economic and environmental concerns and also to lower the dependency on fossil fuels. As a result, many countries have developed their own internal market for the utilization of bioethanol. Almost all of bioethanol is generated from grain or sugarcane currently but other alternative technologies should also be looked into, which can be efficient as well as economical. Many microalgal strains were taken from seawater and examined and experimented for bioethanol production. Some has greater growth rate, i.e., 20–30 dry biomass/m^2/day and greater starch content of more than 20 % dry base. *Chlorella vulgaris* has 37 % starch content, which is very high and hence starch is taken from its cell, saccharified and fermented with yeasts. Ethanol conversion rate is 65 % as compared to the theoretical value. The starch extracted from algae is considered to be an excellent source for the production of ethanol by applying conventional process. Intracellular fermentation of starch under dark anaerobic conditions is examined as an alternative source of production of ethanol. Increased ethanol is obtained from *Chlamydomonas reinhardtii* and Sak 1 extracted from seawater. This process shows mass concentration of ethanol 1 % (w/w). The properties of production of ethanol are observed at the intracellular level with *Chlamydomonas*. The results obtained show that intracellular production of ethanol is easier, simpler, and its energy is lower than the conventional fermentation process of ethanol. If the productivity rate of microalgae can be enhanced, this setup should be effective for the fixation of CO_2 and production of energy (Li et al. 2008). Macroalgae can also serve as a source of renewable biomass used for the production of ethanol. Very little has been done on this issue currently and extensive research is necessary in this area in the future for the progressive utilization of biomass acquired through algae and their wastes products to generate bioethanol fuel which is environment friendly.

7.13 Future Prospects

Sustainable biofuels are required to substitute the petroleum-based transport fuels, which cause climate change and global warning and are also being depleted. Two possible renewable sustainable fuels that can be utilized and have captivated the most attention are biodiesel and bioethanol. Biodiesel and bioethanol extracted from microalgae are the only option for renewable biofuel with the potential to displace fossil fuel without causing any adverse effects to the environment and economy. Production of biofuel through microalgae is superior than biofuel production from oil crops. For example, studies in the U.S. suggests that biodiesel can replace all fuel used for the consumption of transport. It will require 0.53 m^3 of biodiesel yearly at the modern consumption rate. We cannot utilize waste cooking oil, oil crops, and animal fat to realistically state our demands. Biodiesel production through microalgae between 1 and 3 % of the total US area that is used to grow crops would be sufficient in the production of algal biomass that fulfills 50 % of the needs of transport fuels (Courchesne et al. 2009).

Other than biofuel, microalgae can be used to produce large amount and range of bio-products, i.e., medicine, food, cosmetic industry, and have novel applications. Through microalgal approach, we can efficiently heighten the biofuel overall cost-effectiveness. Different developments in technology including advancements in biomass harvesting of microalga, layout of photobioreactors, drying and other several downstream processes are vital fields which can also lead to the increased cost-effectiveness and thus implementation in the commercial market of biofuel by using microalgal strategy (Brennan and Owende 2010).

7.14 Conclusion

Due to the rapid and excessive use of energy in today's world, its demand is increasing day by day. At this time algal biomass could serve as a promising source of renewable energy. Using the above-mentioned processes, we can obtain a large amount of energy from algal biomass. The above discussion gives an insight of how algal biomass can be processed through several processes to finally convert it into energy. Using these processes, we can obtain biogas, bioethanol, biodiesel, and other products. The use of microalgal biomass may also resolve the pollution issues caused by the use of fossil fuel. In short, energy obtained from microalgal biomass can serve as an alternative for the fossil fuel.

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